

# Major and Trace Element Analysis of Natural and Experimental Igneous Systems using LA-ICP-MS

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1811-5209/16/0012-0311\$2.50 DOI: 10.2113/gselements.12.5.311

**L**aser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) enables spatially resolved quantitative measurements of major, minor and trace element abundances in igneous rocks and minerals with equal or better precision than many other in situ techniques, and more rapidly than labour-intensive wet chemistry procedures. Common applications for LA-ICP-MS in the Earth sciences centre on investigating the composition of natural and experimental geological materials, including: analysis of whole rock silicate glasses, flux-free pressed powder tablets and/or fused aliquots of materials; in situ probing of individual minerals, xenocrysts, fluid and melt inclusions, experimental run products, and siderophile-rich micronuggets; and multidimensional chemical mapping of complex (multiphase) materials.

**KEYWORDS:** in situ LA-ICP-MS, trace element, experimental petrology, chemical mapping, spatial resolution

## INTRODUCTION

Major- and trace-element compositions of minerals provide valuable information on a variety of global Earth-system processes, including melting of distinct mantle reservoirs, the growth and evolution of the Earth's crust and the formation of economically viable ore deposits. In the mid-1980s and early 1990s, attempts were made to couple laser ablation (LA) systems to inductively coupled plasma mass spectrometry (ICP-MS) instruments (e.g. Fryer et al. 1995; Jackson et al. 1992). The goal was to develop a rapid, highly sensitive in situ analytical technique to measure abundances and spatial distributions of trace elements in minerals and other geological samples. Elemental analysis using LA-ICP-MS was envisaged as a quicker and less destructive means of chemical analysis (requiring only µg quantities) than labour-intensive sample digestion and solution analysis (requiring mg-levels of material); and it would be a more cost-effective method than secondary ion mass spectrometry (SIMS) for the routine analysis of trace elements from solid samples. Furthermore, it would have lower limits-of-detection than electron probe micro-analysis (EPMA) (e.g. Jackson et al. 1992; Eggins 2003).

Today, LA-ICP-MS systems are becoming increasingly capable and user-friendly (Russo et al. 2013). Improved optics and software (such as the ability to import images and point locations from other instruments) have sped up the process of identifying and locating analytical targets, especially during thin-section analysis. Analyses can now be automated and ICP-MS software is capable

of outputting fully quantitative LA-ICP-MS data. Moreover, hybridized laser ablation systems are now being produced with built-in photon detectors that support laser-induced breakdown spectroscopy (LIBS) and/or laser ablation molecular isotopic spectrometry (LAMIS), enabling trace- and major-element abundances, as well as isotopic ratios, to be measured simultaneously without the need for a traditional internal standard (Russo et al. 2013).

Although methods may vary, LA-ICP-MS techniques have been well-validated and are capable of

producing high-precision and accurate data for a range of geological materials (Jackson 2008; Arevalo et al. 2011; Jenner and O'Neill 2012a; Russo et al. 2013). Nonetheless, the minimization of errors is still a work-in-progress. Here, we summarize the important issues that need to be considered during major- and trace-element LA-ICP-MS analysis, focusing on the advances these techniques have made in areas of igneous and experimental petrology.

## METHODOLOGY AND CHALLENGES FOR ANALYZING GEOLOGIC MATERIALS USING LA-ICP-MS

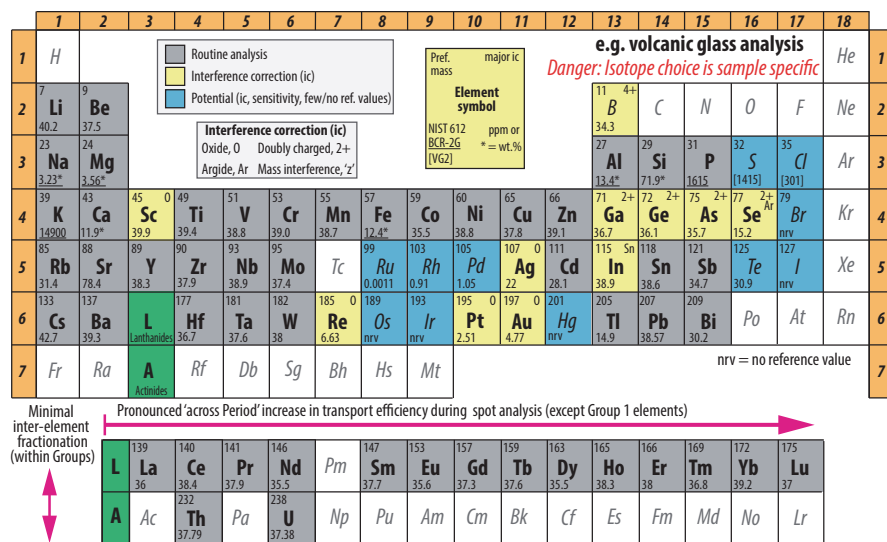
### External Calibration

To quantitate major- and trace-element abundances via LA-ICP-MS techniques typically requires bracketing unknown samples with those of known compositions (external reference materials), in addition to knowing the abundance of one element (e.g. Si or Ca, determined independently by EPMA) in the unknown sample for internal calibration (see Jackson 2008). For external calibration of LA-ICP-MS analyses, only a few materials have sufficiently accurate reference values for >40 elements. The foremost of these are the series of synthetic glasses produced by the (US) National Institute of Standards and Technology Standard Reference Material (NIST SRM), which are doped with trace elements at varying concentrations (e.g. NIST SRM 612) (Fig. 1) and permit the accurate analysis of >60 elements using LA-ICP-MS techniques (Jenner and O'Neill 2012a, b).

Reference glasses have also been made by the laboratory fusion of rock powders to glass, such as various United States Geological Survey (USGS) and Max-Planck-Institut-Dingwell (MPI-DING) glasses. Although valuable for external calibration, the concentrations of some elements in these natural composition reference glasses are extremely low, variable and/or poorly constrained (Jochum et al.

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**FIGURE 1** Annotated periodic table showing the isotopes usable for the analysis of volcanic samples, the likely molecular interferences that will be encountered (exceptions given in Arevalo et al. 2011), and an example of values from the NIST SRM 612, BCR-G or VG-2 reference standards that can be used for external calibration of LA-ICP-MS data. Isotope choices exemplified here do not apply to all materials (e.g.  $^{91}\text{Zr}^{16}\text{O}$  interferences on  $^{107}\text{Ag}$  during analysis of Ag-rich Zr-poor sulphides are inconsequential). REFERENCE MATERIAL VALUES FROM JENNER AND O'NEILL (2012a, b), JOCHUM ET AL. (2011) AND WANG AND BECKER (2014).

2006; Jenner and O'Neill 2012b). Hence, the NIST SRM glasses are currently the most reliable options with respect to calibrating LA-ICP-MS analyses for a broad range of elements. Although heterogeneities in the NIST SRM series glasses have been reported (see Jackson 2008 for overview), such areas can be identified using line scans and then avoided. Interferences and high backgrounds make NIST SRM 612 glass, which has low K and P contents, a poor choice for external calibration (Jackson 2008; Jenner and O'Neill 2012b). Instead, for major rock-forming elements, it is preferable to use well-characterized reference materials of natural compositions, such as the USGS fused glass from powdered basalt from Columbia River (BCR-2G), the Smithsonian National Museum of Natural History (NMNH) natural volcanic glass (VG-2, also referred to as NMNH 111240-52) from the Juan de Fuca Ridge (values given in Fig. 1) or the MPI-DING glasses.

### Laser-Induced Elemental Fractionation (LIEF)

During sample ablation, there is generally a decrease in signal intensity with progressive ablation and decreasing laser pit aspect ratio (e.g. Eggins et al. 1998). The rate of signal decay is faster for some elements (e.g. Ca) than others (e.g. Si), due to what is termed "down-hole" or laser-induced elemental fractionation (LIEF). As a result, measured signal intensity ratios (e.g. Ca/Si) can vary as a function of time and may not be representative of the target material (e.g. Fryer et al. 1995; Eggins et al. 1998; Jackson 2008; Jenner and O'Neill 2012b). Although signal decay can be mitigated by moving the sample stage during laser ablation (i.e. line scans) and producing a trench of constant depth, line scans have been shown to produce greater proportions of large particle sizes ( $>1\ \mu\text{m}$ ) compared to stationary laser pits (Tang et al. 2014), resulting in differential vaporization and ionization of elements in the torch of the ICP-MS and exacerbating LIEF (e.g. Jackson 2008; Tang et al. 2014). Other operational parameters that impact on the distribution of ablated particle sizes reaching the ICP-MS, and ultimately controlling LIEF, include the following: laser wavelength and pulse duration; carrier gas composi-

tion and flow rates; and the optical and physicochemical properties of the sample substrate (see Jackson 2008; Russo et al. 2013; Arevalo 2014). Stoichiometric laser sampling is most closely approached when using femtosecond, as opposed to nanosecond, laser pulses (e.g. Russo et al. 2013; Arevalo 2014).

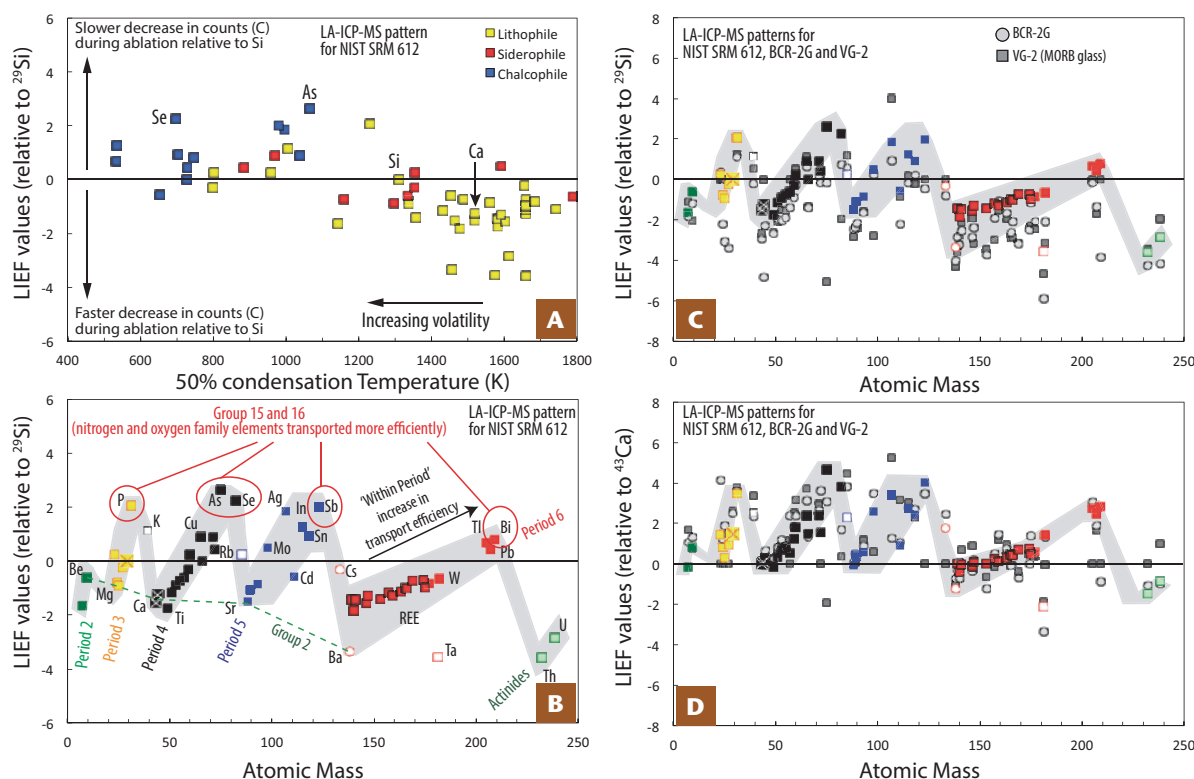
Laser-induced elemental fractionation (LIEF) is commonly attributed to differences in elemental atomic mass, first ionization potential, condensation temperature and geochemical behaviour (i.e. lithophile, chalcophile or siderophile) (see Jackson 2008 for detailed overview). For example, there is a broad increase in LIEF values with decreasing element volatility (Fig. 2A), and chalcophile elements typically exhibit positive LIEF values, whereas lithophile and siderophile elements typically have negative LIEF values compared to  $^{29}\text{Si}$ . However, when LIEF indices are grouped

according to their respective Period on the Periodic Table and plotted according to atomic mass, a striking pattern emerges (Jenner and O'Neill 2012b) (Fig. 2B). Exempting Group 1 elements, there is a systematic increase in LIEF values from left to right (Group 2 to Group 16; Fig. 2B) across each of the Periods; these patterns cannot solely be attributed to increases in atomic mass, because, for example, elements from Group 2 (Be, Mg, Ca and Sr) have comparable LIEF values despite large differences in atomic mass. Rather, the zigzag LIEF pattern observed across the Periodic Table appears to be controlled by a combination of volatility, electronegativity and the first ionization potential of a given element. It is important to be aware of how elements respond differently during laser-ablation, because documenting such factors ultimately contributes to advances towards improving the accuracy and precision of reported LA-ICP-MS analyses (e.g. Jackson 2008; Jenner and O'Neill 2012b), as discussed below.

### Matrix Matching and Internal Calibration

The photon absorption behaviour of different sample materials is influenced by the optical, chemical and physical properties of the target material (e.g. Jackson 2008; Arevalo 2014). As a result, the synthetic NIST glasses show different ablation characteristics from natural geological samples (e.g. Jenner and O'Neill 2012b). Non-matrix-matched calibration of LA-ICP-MS data requires that potential differences in the magnitude of LIEF (i.e. the total range in LIEF between the Group 2 and Group 16 elements) and/or subtle differences in the LIEF patterns themselves between external reference materials and unknowns be assessed critically.

FIGURES 2C and 2D compare LIEF patterns normalized to  $^{29}\text{Si}$  and  $^{43}\text{Ca}$ , respectively, during analysis of NIST SRM 612, of BCR-2G and of VG-2. When  $^{43}\text{Ca}$  is used as an internal standard (Fig. 2D), LIEF patterns produced during ablation of BCR-2G, VG-2 and NIST SRM 612 are comparable. If, however,  $^{29}\text{Si}$  is used for internal calibration, the LIEF patterns for NIST SRM 612 are offset to systematically higher values compared to those produced during ablation of VG-2 and BCR-2G (Jenner and O'Neill 2012b). Hence, when using  $^{29}\text{Si}$  for internal calibration, a correction is required to account for the differences in ablation characteristics of Si relative to the other elements. But this correction is not needed if  $^{43}\text{Ca}$  is used as the internal standard. Considering the regularity of the zigzag LIEF pattern for a given material over extended periods of time (see Jenner and O'Neill 2012b), once the LIEF patterns between external reference materials and unknowns are



**FIGURE 2** Laser-induced element fractionation mean values [ $LIEF = 1,000 \cdot (d[C_x/C_{IS}]/dt)/[C_x/C_{IS}]$ ], where C are the counts for a given 'unknown' element (x) or the 'known' internal standard (IS)] plotted (A) versus 50% condensation temperatures (K), which are commonly used as a proxy for volatility, and (B–D) against atomic mass. (A) LIEF values show a broad increase with decreasing volatility of a given element. Excluding Group 1 elements, Si-normalized LIEF values (B–C) and Ca-normalized LIEF values (D) show a systematic zigzag pattern when compared against atomic mass. For Si-normalized LIEF (C), there is an offset between NIST SRM 612 with VG-2 and BCR-2G. In contrast, for Ca-normalized LIEF (D), values for the three element standards NIST SRM 612, VG-2 and BCR-2G are typically within error. Note: the scatter in LIEF values for geological materials can be attributed to the low contents of many trace elements (e.g. As, Ag and W) in BCR-2G and VG-2. FIGURE MODIFIED WITH PERMISSION OF JOHN WILEY AND SONS FROM JENNER AND O'NEILL (2012b).

constrained, element-specific matrix corrections can be implemented to increase accuracy.

### Irksome Interferences

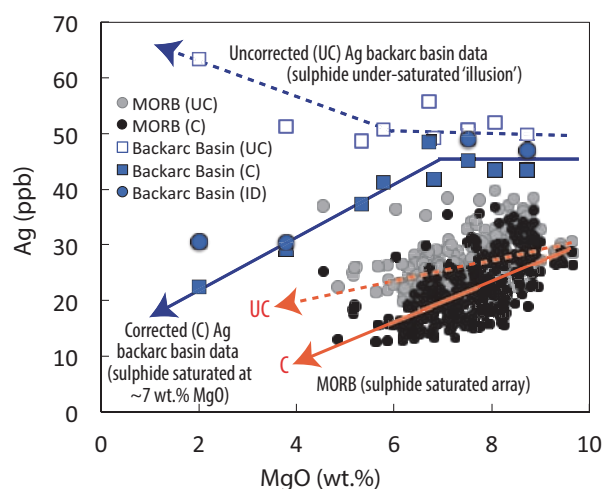
Most ICP–MS instruments rely on quadrupole mass analysers that only provide unit mass resolution. A challenge to accurate data quantitation is the identification of which isotope of a targeted element is least likely to suffer from competing signals (interferences) from elemental or molecular species (e.g. oxides, argides or doubly charged ions) sharing similar mass-to-charge ratios as the selected isotope. Using the isotopes of FIGURE 1, the contents of ~50 elements can be determined in mid-ocean ridge basalt (MORB) glasses to within the expected uncertainties of the LA–ICP–MS technique, without correction for interferences. In contrast, the magnitude of interference complications during LA–ICP–MS analysis for other elements (e.g. Sc, As and Se) (Fig. 1), are significant. Interferences can be measured and corrected for (Jenner and O'Neill 2012b); they can be resolved by increasing the mass resolution using tuneable sector field instruments (e.g. Arevalo et al. 2011; Arevalo 2014); and/or they can be attenuated using a collision/reaction cell, which is located between the ion optics and mass analyser of modern low-resolution instruments (e.g. Arevalo 2014; Chew et al. 2014).

The LA–ICP–MS analysis of Ag in geological materials provides an example of the importance of accounting for isobaric interferences when one needs accurate data quantitation. The correction for the combination of  $^{90}\text{Zr}^{17}\text{O}$  and  $^{91}\text{Zr}^{16}\text{O}$  interferences on  $^{107}\text{Ag}$  during the analysis of a mid-ocean ridge basalt (MORB) appears minor on the plot of Ag versus MgO (Fig. 3); both interference-corrected and interference-uncorrected MORB datasets show a decrease in Ag contents because MORBs are sulphide-saturated during differentiation (Jenner et al. 2012). However, without the interference correction, the increase in Ag with decreasing MgO of the backarc basin suite could be used to argue, erroneously, that the melts are sulphide under-saturated: the corrected trend shows that sulphide saturation is actually achieved at ~7 wt% MgO (Jenner et al. 2012).

## APPLICATION OF LA–ICP–MS

### Silicate Glasses and Melt Inclusions

Seafloor volcanic glasses are valuable to geochemists because their homogeneous nature permits analysis using in situ techniques, such as LA–ICP–MS. In situ techniques enable the determination of 'liquid' compositions, which are critical for obtaining accurate liquid lines of descent for cooling magmas (e.g. Ag versus MgO on Fig. 3). Databases



**FIGURE 3** Plot of Ag versus MgO for global mid-ocean-ridge basalt (MORB). The magnitude of the  $^{90}\text{Zr}^{17}\text{O}$  and  $^{91}\text{Zr}^{16}\text{O}$  interference correction appears minor, and both interference corrected (C) and uncorrected (UC) data could be used to argue that the melts were sulphide-saturated (i.e. Cu decreases with decreasing MgO). However, lack of an interference correction would result in a major over-estimate of the Ag contents of the evolved (low MgO) backarc basin samples and would be used to erroneously conclude that the melts remained sulphide-under-saturated during differentiation. DATA FROM JENNER AND O'NEILL (2012A) AND JENNER ET AL. (2012); INTERFERENCE CORRECTIONS CONFIRMED USING UNPUBLISHED ISOTOPE DILUTION (ID) DATA FROM MARY HORAN (DEPARTMENT OF TERRESTRIAL MAGNETISM, CARNEGIE INSTITUTION OF WASHINGTON).



of analyses of global MORB glasses (e.g. PetDB: <http://www.earthchem.org/petdb>, or GEOROC: <http://georoc.mpch-mainz.gwdg.de/georoc/>) are typically restricted to  $\leq 40$  elements and/or are compilations of data collected using a variety of techniques. However, LA-ICP-MS analysis of volcanic glasses offers the opportunity to measure with a single instrument the contents of  $>60$  major and trace elements (Fig. 2), including many lesser-analysed elements whose behaviour during igneous processes remains poorly constrained (Jenner et al. 2012; Jenner and O'Neill 2012a).

Melt inclusions are mineral-hosted droplets of silicate melt that became trapped during mineral growth. They record information about the pre-eruptive history of silicate melts, which is especially useful when they are discovered in minerals that form crystalline plutonic rocks. Based on comparisons with SIMS data, both the precision and accuracy of LA-ICP-MS analysis of  $\sim 30\text{--}50\text{ }\mu\text{m}$  melt inclusions can be better than 10%–15% at the  $2\sigma$  limit (Kent 2008). Moreover, LA-ICP-MS techniques permit the analysis of transition metals and of chalcophile and siderophile elements in melt inclusions, which are commonly beyond the capabilities of SIMS and/or are notoriously difficult and time consuming to make using whole-rock techniques (e.g. Kent 2008; Wang and Becker 2014). Combined EPMA, SIMS, X-ray absorption near-edge structure (XANES) and LA-ICP-MS datasets for melt inclusions (e.g. Kelley and Cottrell 2012) have revealed key new insights into the genesis of mid-ocean ridge magmas and of convergent margin magmas (e.g. linear correlations between Ba/La with  $\text{Fe}^{3+}/\Sigma\text{Fe}$ , S and  $\text{H}_2\text{O}$ ).

### Whole Rock Analysis

Unfortunately, volcanic glasses are quite rare and most rock samples on the Earth's surface represent complex mixtures of liquids and minerals. One traditional method to analyse whole-rock samples is to dissolve the rock in acid and subsequently analyse the composition of the resulting solution. However, many whole-rock geological samples, such as granites, contain phases that are resistant to acid attack (e.g. Nb- and Ta-bearing rutile, and Zr- and Hf-bearing zircon). Consequently, solution-derived data for these elements can be of inconsistent quality if complete sample digestion is not achieved. Another method used to study whole rocks involves complete melting of the sample. This can be achieved using methods employed to form glasses from powdered rock samples either with a lithium borate flux (e.g. Eggins 2003) or without (e.g. Jochum et al. 2006). Such sample preparation methods enable subsequent analysis via LA-ICP-MS. However, sample melting risks contamination from addition of flux and/or from interaction of the silicate melt with the crucible (typically made of Pt) that is used to heat the sample. Further, analysis of lithium borate glasses may pollute the torch of the ICP-MS with Li and B, contributing to long-term 'memory effects' and compromising the limits of detection of both elements. The LA-ICP-MS analysis of nano-particulate powdered samples pressed into tablets obviates the potential for contamination associated with addition of lithium borate fluxes and/or fusion in Pt crucibles, and provides comparable levels of precision and accuracy to LA-ICP-MS analyses of volcanic glasses (Garbe-Schönberg and Müller 2014). Another advantage of using pressed-powder versus fused-glass techniques is that samples retain their volatiles, as no sample heating is required (e.g. the MPI-DING glasses have lost virtually all S during heating) and the optimum concentrations of trace elements are maintained because of the lack of dilution by the flux

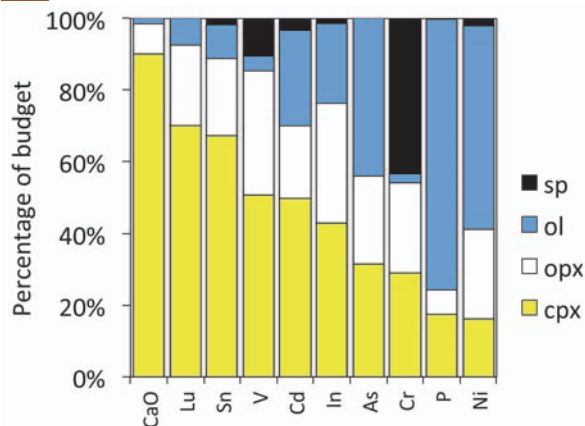
### Mineral and Partition Coefficient Analysis

Many natural materials host a range of different minerals, melts and fluid inclusions, resulting in heterogeneous distributions of elements on a variety of scales: from those visible optically to those requiring chemical mapping to identify. A major advantage of LA-ICP-MS techniques is the ability to analyse individual minerals with minimal sample processing and to select representative ablation signal intervals during data processing. This latter requirement is needed for two reasons: first, to filter signals from impurities, which allows meaningful data to be generated from inclusion-bearing ablation volumes (see Jackson 2008 for detailed discussion); second, to obtain data for multiple mineral species from a single analysis (e.g. Patten et al. 2013). Modern laser ablation systems provide analysts with the ability to ablate material using a variety of ablation shapes. Rectangular ablation shapes can be used to improve the resolution of geochemical profiles across zoned mineral grains relative to profiles obtained using circular ablation shapes (e.g. Qian et al. 2010). Because of these advantages, LA-ICP-MS analyses of various minerals are increasingly populating online mineral databases, such as those hosted by PetDB and GEOROC.

On a mineral-by-mineral basis, combined EPMA and LA-ICP-MS datasets have permitted the first comprehensive investigations of the distributions of nearly 60 elements in the layered igneous intrusion of the South African Bushveld Igneous Complex (Tanner et al. 2014). These datasets have revealed new details regarding magma recharge events and on extensive sub-solidus equilibration (diffusion) during prolonged cooling of the Bushveld Igneous Complex. The application of different LA-ICP-MS methods has probably led to the biggest advance in our understanding of the behaviour of the chalcophile and siderophile elements. For example, Howell and McDonald (2010) provide an excellent review of the numerous ways that LA-ICP-MS analysis of the concentrations of platinum-group elements (PGE) in sulphide minerals has allowed the behaviour of precious metals to be constrained to an extent not previously possible using other micro-analytical techniques. Line scans using LA-ICP-MS across sulphide globules hosted in MORB glasses have been used to provide the most comprehensive list of the natural partition coefficients ( $D$ ) for chalcophile and siderophile elements (e.g.  $D_{\text{Cu}}^{\text{sulphide melt/silicate melt}}$ ) available in the literature (Patten et al. 2013). Additionally, LA-ICP-MS analyses of fertile mantle xenoliths have demonstrated that silicate minerals host the bulk of many of the chalcophile/siderophile elements in the mantle (e.g. Sn, Cd, In, As, Ni) (Fig. 4).

### Chemical Mapping

Chemical mapping of individual minerals and multiphase assemblages on the micrometre scale can be achieved via LA-ICP-MS. Combining data from parallel line scans across mineral grains can be used to provide 2-D compositional maps and progressive rescanning of surfaces can be used to provide 3-D chemical maps (e.g. Woodhead et al. 2007; Ulrich et al. 2009; Peng et al. 2012; Paul et al. 2014). Chemical mapping of minerals using LA-ICP-MS has revealed geochemical details, such as non-concentric zoning of Tb and Yb in garnet (Ulrich et al. 2009) that might not be obvious using single line scans across mineral grains. Peaks in Th, which would complicate the use of bulk radiogenic dating methods (Ulrich et al. 2009), have been used to image minute apatite and zircon inclusions in specific regions of a host garnet. Furthermore, LA-ICP-MS imaging permits the distribution of trace elements in multiphase samples (e.g. gabbros) to be characterised, thereby allowing petrologists to define trace element systematics



**FIGURE 4** The relative distributions of elements between four rock-forming silicate minerals within fertile lherzolites (mantle xenoliths). Elements typically referred to as 'chalcophile' are partitioned into the silicates clinopyroxene (cpx), olivine (ol) orthopyroxene (opx) and spinel (sp). Additionally, unlike the majority of trace elements, the bulk partitioning of P is controlled by olivine and not clinopyroxene. DATA DERIVED FROM WITT-EICKSCHEN ET AL. (2009).

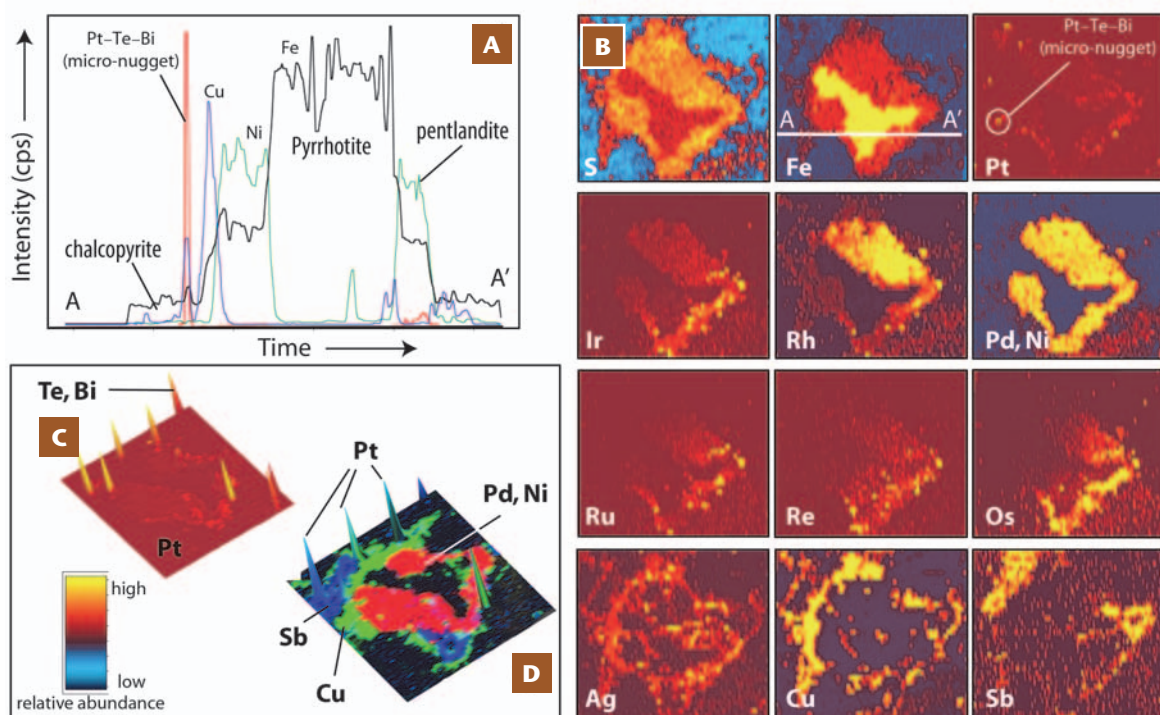
in more detail than 'comparable' information derived from the less sensitive EPMA method and at a fraction of the cost of SIMS analysis (Paul et al. 2014).

### LA-ICP-MS and Experimental Petrology

Essential to experimental petrology is the ability to analyse run products (minerals and glasses) that range in size from <10 µm up to >100 µm. Because of the relatively low sensitivity of EPMA, experimental petrologists grew accustomed to doping their experiments with elemental concentrations unlikely to occur in natural systems. This approach is limited, however, by the potential for high doping levels to dramatically change the properties of the system under investigation. By offering spot sizes from just a few microns up to hundreds of microns in diameter, LA-ICP-MS allows experimental calibration of equilibria at trace concentrations in the same way that experimental petrologists have traditionally used EPMA for major elements (e.g. Mallmann and O'Neill 2009). Additionally, because

experimental petrologists frequently need numerous tests to establish an appropriate experimental design, the speed and cost of analysis makes LA-ICP-MS preferable to SIMS. Furthermore, on account of their delicate nature, experimental products are commonly impregnated with epoxy resin prior to opening and polishing of experiments, which compromises the ability to achieve low vacuums during SIMS analysis. Hence, LA-ICP-MS has become an essential part of the experimental petrologist's toolkit.

As an example, LA-ICP-MS analysis has revolutionized our understanding of the highly siderophile elements (HSEs, such as Re and Au), which have a strong affinity for iron and tend to form small metal particles (~0.05 µm in radius) that are often referred to as 'micronuggets' (Ertel et al. 1999). Prior to the identification of HSE-rich micronuggets, which were discovered using LA-ICP-MS techniques (manifest as spikes in time-resolved data, FIG. 5A), there had been strong misconceptions regarding both the solubility and speciation of the HSEs in silicate melts (Ertel et al. 1999) and, in turn, our understanding of processes such as how the Earth's core formed. Such micronugget elemental 'spikes' are commonly removed from time-resolved spectra during data reduction. However, data filtering techniques need to be considered carefully to ensure that valuable information is not lost. For example, Ulrich et al. (2009) demonstrated that laser imaging could be used to place constraints on the distribution of chalcophile and siderophile elements in a composite sulphide grain from the Merensky Reef (part of the Bushveld Igneous Complex; FIG. 5). The Pt-Te-Bi micronuggets are restricted to the thin Cu-rich chalcopyrite rim of the composite sulphide grain, or are at its grain boundaries (FIG. 5C AND 5D), as opposed to the central Ni-rich pentlandite and Fe-rich pyrrhotite portions of the composite sulphide grain. The micronugget occurrence appears to be linked to the partial replacement of pyrrhotite and pentlandite by chalcopyrite. Production of chemical maps might provide clues to the nature and distribution of micronuggets in experimental runs and, potentially, how to improve experimental designs. Additionally, Ulrich et al. (2009) demonstrated that Ni and Pd show homogeneous distributions, whereas the concentrations of Pt, Ru, Rh, Re, Os and Ir are highly variable between neighbouring pentlandite grains (FIG. 5B), which is contrary to typical



**FIGURE 5** Demonstration of the capabilities of LA-ICP-MS for laser imaging of sulphide minerals and the various ways that LA-ICP-MS data can be depicted. All four plots refer to the same area. (A) Time-resolved intensity plots of line scans across composite mineral grains. (B) Twelve 2-D compositional maps for 13 elements. (C-D) Two 3-D compositional maps, which can be used to 'pull out' chemical information (e.g. the distributions of elusive micronuggets) from time-resolved LA-ICP-MS data. ADAPTED FROM ULRICH ET AL. (2009).

categorizations that tend to group Pd with Rh and Pt. Thus, the application of laser imaging to the analysis of both natural and experimental igneous rocks is very likely to continue to further our understanding of the range of geological processes that went into forming these rocks.

## FUTURE ADVANCES

The ability to accurately, precisely and rapidly analyse the contents of >60 elements in a range of samples (including whole rocks, minerals, volcanic glasses, melt inclusions, fluid inclusions, and experimental run products), and all at relatively low costs, have contributed to the growing popularity of LA-ICP-MS since its inception in 1985. Recent advances in chemical mapping suggest that the scientific impact of the technique, especially when addressing questions pertinent to understanding igneous processes, will only continue to grow. However, user-friendly and

fully quantitative laser imaging of the distribution of major and trace elements in geological materials is still a 'work in progress'. Future advances that would be invaluable to studies of both natural and experimental igneous systems include the full integration between various in situ imaging techniques (e.g. SIMS, EMPA and LA-ICP-MS).

## ACKNOWLEDGMENTS

Hugh O'Neill, Charlotte Allan and Ashley Norris are thanked for comments during preparation of the manuscript. Thomas Ulrich is thanked for kindly giving permission to reproduce his figure (Fig. 5). Mary Horan is also thanked for permitting us to use her unpublished Ag data. Paul Sylvester, Simon Jackson, Bernie Wood and two anonymous reviewers are thanked for giving up their time to provide helpful, concise and detailed reviews and editorial advice. ■

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